1 OXONIUM COMPOUND FORMATION BY ALCOHOL IN AQUEOU S SOLUTION

11 THE HYDRATION OF ACETYLENE

by

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I OXONIU M COMPOUND FORMATION BY ALCOHOL IN AQUEOUS SOLUTION

SUMMARY

1. The distribution of alcohol between benzene and aqueous solutions of (1) sulfuric acid, (2) sodium sulfate, and (3) mixtures of perchloric acid and sodium perchlorate has been studied.

2. Apparent values of equilibrium constants for the formation of oxonium salts in aqueous solutions have been calculated.

INTRODUCTION

It is well known that alcohols, ethers, and other so-called neutral organic compounds containing oxygen actually show very weak basic properties, forming unstable addition products (oxonium salts) with acids. This is due to the tendency of a free proton to attach itself to an unshared electron pair, according to the general scheme

$$ROR' + H^+ \rightleftharpoons \overset{H}{ROR}^+$$

Oxonium compound formation by ethyl alcohol was demonstrated by Maass and McIntosh[1], who investigated the melting-point curves of the systems alcohol-hydrogen bromide and alcohol-bromine. The curve for the former system shows a maximum of -28°C at the point at which the composition corresponds to the product $C_2H_5OH \cdot HBr$. The shape of the curve indicates appreciable decomposition at this point. It would be expected that at higher temperatures, e.g., room temperature, the decomposition would be quite large and that in aqueous solution oxonium compounds would be formed only to a small extent, due to the water molecule competing with the alcohol molecule for the proton

$$C_2H_5OH_2^+ + H_2O \rightleftharpoons C_2H_5OH + H_3O^+$$

The effect of alcohol on the acidic and dissociation constants of acids and acid-base indicators has been investigated by several workers.[2-10] Brönsted[11] reviews the work done in this field and calculates that alcohol is about 330 times

as weak a base as water. Kolthoff[10] calculates that this figure should be about 400.

The purpose of this research was to measure, if possible, the equilibrium in the formation of oxonium compounds by alcohol in aqueous solution.

THEORY

If alcohol is distributed between an insoluble organic solvent, such as benzene, and an aqueous solution of an acid, and between the organic solvent and a neutral solution of a salt of the acid, the concentration of the alcohol in the organic solvent being kept constant, thus keeping the activity of the alcohol constant, any difference in the amount of alcohol found in the two aqueous phases must be due to the formation of $C_2H_5OH_2^+$, provided that the concentration of the salt is such that the activity coefficients of the alcohol in the two aqueous phases are the same. We have, then

$$\frac{C_{EtOH(W)}}{C_{EtOH(B)}} = r_n \qquad (1)$$

$$\frac{C_{EtOH(W)} + C_{EtOH_2^+}}{C_{EtOH(B)}} \quad r_a \qquad (2)$$

where $C_{EtOH(W)}$ is the concentration of free alcohol in the aqueous phase, $C_{EtOH(B)}$ is the concentration of alcohol in the benzene phase, $C_{EtOH_2^+}$ is the concentration of oxonium ion, r_n is the distribution ratio of alcohol between benzene and the neutral solution and r_a is the distribution ratio between benzene and the acid solution.

In the acid phase we have the following requilibrium

$$C_2H_5OH + H_3O^+ \rightleftharpoons C_2H_5OH_2^+ + H_2O$$

the constant K, for which is given by the expression

$$\frac{C_{C_2H_5OH_2^+} \times \alpha_{H_2O} \times \gamma_{C_2H_5OH_2^+}}{C_{C_2H_5OH(W)} \times C_{H_3O^+} \times \gamma_{C_2H_5OH(W)} \times \gamma_{H_3O^+}} = K \qquad (3)$$

where $C_{EtOH(W)}$ and $C_{EtOH(B)}$ are as above, $C_{H_3O^+}$ is the concentration of hydrated hydrogen ion, α_{H_2O} is the activity of the water, and $\gamma_{EtOH(W)}$, $\gamma_{EtOH_2^+}$, and $\gamma_{H_3O^+}$ are the respective activity coefficients. According to the Brönsted theory K is related to the basic constant $K_{B(EtOH)}$ of alcohol and the basic constant of water $K_{B(H_2O)}$ by the equation

$$K_{B(EtOH)} = K \cdot K_{B(H_2O)} \qquad (4)$$

From (3) we have

$$C_{C_2H_5OH_2^+} = KC_{C_2H_5OH(W} \quad C_{H_3O^+} \frac{\gamma_{C_2H_5OH(W)} \gamma_{H_3O^+}}{\alpha_{H_2O} \times \gamma_{C_2H_5OH_2^+}} \qquad (5)$$

From (1), (2) and (5) we have

$$r_a = r_n \left[1 + KC_{H_3O^+} \frac{\gamma_{EtOH(W)} \times \gamma_{H_3O^+}}{\alpha_{H_2O} \times \gamma_{EtOH_2^+}} \right] \qquad (6)$$

Equation (6) gives a relation between K, the distribution ratios, the hydrated hydrogen ion concentration the activity of the water, and the activity coefficients of the alcohol, oxonium ion, and hydrated hydrogen ion. It shows that the distribution ratio should be independent of the total alcohol concentration and that any change in distribution ratio at constant hydrated hydrogen ion concentration is due to changes in activity coefficients.

EXPERIMENTAL

It is evident that, in order that changes in distribution ratio may really indicate oxonium compound formation, it is necessary that the activity coefficients of the alcohol should be the same in the acid solution as in the neutral solution with which it is compared. In order to calculate accurately the value of K there is needed in addition the absolute values of the activity coefficients and the activities of the water, or of the quantity

$$\frac{\gamma_{EtOH(W)} \times \gamma_{H_2O^+}}{\alpha_{H_2O} \times \gamma_{EtOH_2^+}}$$

The necessary data is not available, but it was hoped that by means of certain approximations, results of some significance could be obtained.

Two series of experiments were made. In the first of these alcohol was distributed between benzene and aqueous sulfuric acid solutions of varying concentration and between benzene and sodium sulfate solutions. In the second series alcohol was distributed between benzene and aqueous solutions of perchloric acid and of mixtures of perchloric acid and sodium perchlorate, the total concentration of electrolyte being kept constant.

PREPARATION OF MATERIALS AND SOLUTIONS. All materials with the exception of the benzene were of c.p. grade.

Pure benzene was prepared as follows: About 2½ liters of a good grade of commercial benzene was placed in a 5-liter balloon flask provided with a motor-driven glass stirrer. About 200 ml. concentrated tech. sulfuric acid was added, and the mixture was stirred for three hours. When the benzene gave no positive test for thiophene with isatin, the sulfuric acid was drawn off and the benzene was washed three times with water. A solution of 250g. tech. sodium dichromate, and 100 ml. concentrated sulfuric acid in 100 ml. water was added. A reflux was attached to the flask, and the latter was immersed in a water bath at 45°- 55°. The mixture was well stirred for about 10 hours. The benzene was distilled off and redistilled from 15g. sodium carbonate. It was tested for reducing substances by running a blank as in the determination of alcohol in benzene. Blanks for 10 ml. benzene were 0.01, 0.00, 0.02 ml. 0.1N thiosulfate.

The various standard solutions were prepared and standardized in the usual ways. Sulfuric acid and perchloric acid were standardized against recrystallized borax, using methyl orange.(IR) Sodium hydroxide solutions were standardized against standard sulfuric acid. Neutral potassium dichromate was prepared by weighing out the pure dried salt. Potassium dichromate in 50 vol. % sulfuric acid was standardized against thiosulfate which had been first standardized against the neutral potassium dichromate. The thiosulfate was stabilized

by the addition of 1 vol. % amyl alcohol. Acid ferrous sulfate was standardized against the neutral potassium dichromate. Standard sodium sulfate solution was prepared by drying the pure anhydrous salt for several hours at 120°- 130° and weighing out the desired amount into a volumetric flask. The standard alcohol solution was prepared by treating c.p. absolute alcohol with a small amount of clean metallic sodium, distilling in carefully dried apparatus protected from atmospheric moisture, and weighing the anhydrous product into a volumetric flask.

DETERMINATION OF ALCOHOL. Various investigators have recommended the chromic acid oxidation method for alcohol, especially for minute amounts, or when the volume of the solution is too small for densimetric methods. The conditions recommended vary, however. Budde[13], Martini and Nourrisson[14], Chabot[15], Nicloux[16], and Mayer[17], recommend heating to some extent, either in a closed or open vessel. Mayer suggests the use of H_3PO_4 instead of sulfuric acid. Semichon and Flanzy[19] recommend oxidation in the cold in 66° Be H_2SO_4. Smith[20] and Liverside[21] also provide for oxidation in the cold. Jerome and Pepin[22] use an approximate method for minute amounts by adding to a hot solution of potassium dichromate containing 50% sulfuric acid and titrating the excess potassium dichromate with standard alcohol solution.

The procedure first adopted and used in obtaining some of the data is as follows: A volume of the standard potassium dichromate solution judged to be 5-10 ml. in excess of that required to oxidize the alcohol to acetic acid is run into a flask from a burette and an equal volume of concd. sulfuric acid is carefully added, with cooling in an ice bath. The sample to be analyzed is then run into the flask, which is then tightly stoppered. The contents are then swirled. If the sample is a benzene solution of alcohol, the contents are swirled at frequent intervals. In any case, at least one hour is allowed for the oxidation. After complete oxidation the flask is opened, 3 ml. of 85% phosphoric acid is added, and a slight excess of ferrous sulfate is run in from a burette.

Three drops of diphenylamine indicator is added, and potassium dichromate is added from a burette to the first permanent intense blue-violet color, the final adjustment is made deliberately, using both ferrous sulfate and potassium dichromate. The volume of potassium dichromate corresponding to the ferrous sulfate is calculated and subtracted from the total potassium dichromate; 0.05 ml. is also subtracted for the oxidation of the indicator. The remainder corresponds to the potassium dichromate used in oxidizing the alcohol to acid.

The procedure was subsequently modified as follows: Instead of adding a volume of concentrated sulfuric acid equal to that of the potassium dichromate solution before adding the sample to be analyzed, the standard dichromate solution was made up containing about 50 vol. % concentrated sulfuric acid. Liverside[21] recommends 60 vol. % of sulfuric acid, but 45 - 50 vol. % was found satisfactory for this work. Due to the high viscosity of the solution, it could not be satisfactorily measured out volumetrically, and so a weight burette was used. Instead of determining the excess dichromate in the presence of the benzene, the benzene was removed by means of a separatory funnel, the solution being first diluted to such a volume that possible losses of dichromate would be negligible. The excess dichromate was determined iodometrically instead of with acid ferrous sulfate.

To test the method 10.00 ml. samples of an aqueous solution of alcohol (0.03735f. in EtOH) were analyzed. With no benzene present 14.88 and 14.86 ml. of 0.1004N $K_2Cr_2O_7$ were

used, corresponding to 99.8% and 99.6%, respectively. With 25 ml. of benzene added, 14.87 and 14.88 ml. of potassium dichromate were used, corresponding to 99.7% and 99.8%, respectively.

DISTRIBUTION EXPERIMENTS. The desired amount of sulfuric acid, sodium sulfate, or perchloric acid and carbonate free sodium hydroxide was pipetted into a 50 ml. volumetric flask (a burette protected from air was used for the sodium hydroxide). Alcohol was added, and the solution made up to the mark. After thorough mixing, the solution was poured into a clean and dry oil sample bottle, 35 ml. of benzene was added, and the bottle was stoppered and shaken in a thermostat at 25.00 ± 0.05°C for periods varying from a few hours to several days. The bottles were then left quietly until separation of the phases was complete. Samples were then drawn for analysis. The benzene samples were analyzed directly, but the aqueous samples were diluted in volumetric flasks and samples of the diluted solutions taken for analysis. Density of the aqueous phases were also determined in most cases. Samples were also drawn for titration with sodium hydroxide.

RESULT AND DISCUSSION

The data on the distribution of alcohol between benzene and aqueous sulfuric acid solutions are given in Table 1; that for the distribution of alcohol between benzene and sodium sulfate solution in Table 2; and that for alcohol between benzene and mixtures of perchloric acid and sodium perchlorate at the constant total electrolyte concentration at 2N in Table 3.

In Tables 1 and 2 the first column gives the experiment number, the second gives C, the electrolyte concentration in mols per liter; the third gives the activity of the electrolyte in pure water solution at the corresponding concentration;; the fourth gives Wt $_{EtOH(B)}$ the weight of alcohol per liter of benzene solution; the fifth gives Wt $_{EtOH(A)}$ the weight of alcohol per liter of aqueous solution; and the sixth gives the distribution ratio r = Wt $_{EtOH(A)}$ /Wt $_{EtOH(B)}$

It is to be noted that some experiments were made with the total aqueous alcoholic concentration at 27.7 - 30.4g per liter, while others (marked with an asterisk in the table) were made with alcoholic concentration from 56.1 - 60.59 per liter. This was done in order to observe the effect of varying alcohol concentration.

TABLE 1

Distribution of Alcohol between Benzene and Sulfuric Acid Solutions at 25

No.	$C_{H_2SO_4}$	$\alpha_{H_2SO_4}$	$Wt_{EtOH(B)}$	$Wt_{EtOH(A)}$	r_a
4	0.2000	0.0488	1.557	29.72	19.09
5	0.2000	0.0488	1.542	29.69	19.25
6	0.4000	0.0766	1.579	28.42	18.00
7	0.4000	0.0766	1.618	29.16	18.02
8	0.402	0.0769	1.660	30.36	18.29
9	0.401	0.0767	1.685	30.40	18.04
10*	0.402	0.0769	3.498	60.46	17.28
11*	0.401	0.0767	3.507	60.26	17.18
12	0.5000	0.0890	1.556	28.43	18.27
13	0.6034	0.102	1.715	30.33	17.69
14	0.700	0.114	1.571	27.71	17.64
15	0.700	0.114	1.613	28.22	17.50
16	0.702	0.114	1.614	28.83	17.86
17	0.950	0.143	1.676	28.84	17.21
18	0.952	0.143	1.711	29.00	16.95
19*	0.953	0.143	3.573	57.52	16.10
20*	0.952	0.143	3.571	57.60	16.13
21	0.962	0.144	1.748	29.52	16.89
22	0.962	0.144	1.702	29.36	16.25
23	1.905	0.281	1.840	28.71	15.60
24	1.911	0.282	1.846	28.79	15.60
25*	1,910	0.282	3.757	57.06	15.19
26*	1.912	0.282	3.715	50.09	15.10

TABLE 2

Distribution of Alcohol between Benzene and Sodium Sulfate Solutions at 25.00

No.	$C_{Na_2SO_4}$	$\alpha_{Na_2SO_4}$	Wt $_{EtOH(B)}$	Wt $_{EtOH(A}$	r $_n$
1	0	0	1.422	29.09	20.46
2	0	0	1.430	29.08	20.48
3	0	0	2.892	58.03	20.16
27	0.200	0.0566	1.755	29.62	16.88
28	0.200	0.0566	1.708	28.72	16.81
29	0.400	0.0908	2.052	29.19	14.23
30	0.400	0.0908	1.982	28.43	14.35
31	0.500	0.1045	2.090	27.91	13.34
32	0.500	0.1045	2.141	28.37	13.25
33	0.600	0.1188	2.292	27.95	12.20
34	0.600	0.1188	2.270	27.70	12.21
35	0.800	0.1486	2.745	28.11	10.24
36	0.800	0.1486	2.727	28.00	10.27

Fig. 1 shows the distribution ratios plotted against electrolyte concentration. Fig. 2 shows distribution ratios plotted against electrolyte activities, these activities being for the electrolyte in pure water at the same concentration. Using values of r_a and r_n read from Fig. 3 at activities of 0.05, 0.10, 0.15, and letting $C_{H_3O^+}\ \gamma_{H_3O^+}$ be represented by twice these activities, the values have been calculated for $\frac{\gamma_{EtOH(W)} \times \gamma_{H_3O^+}}{\alpha_{H_2O} \times \gamma_{EtOH_2^+}}$ K. These values are given in Table 4. The wide variation of these values indicate that either $\gamma_{EtOH(W)}$ increases rapidly with increasing electrolyte activity or that $\frac{\gamma_{EtOH(W)} \times \gamma_{H_3O^+}}{\alpha_{H_2O} \times \gamma_{EtOH_2^+}}$ decreases rapidly. Both may take place. Furthermore, the effect of alcohol on the activities of the electrolytes are not known.

It will be seen from Table 1 and Figs. 1 and 2 that changing total alcohol concentration has a larger effect on distribution ratio than is to be expected if it is assumed that such effect is due solely to decreasing the concentration of hydrated hydrogen ion. It therefore follows that the effect of alcohol on the activity coefficients is large.

If we set $\frac{\gamma_{EtOH(W)} \times \gamma_{H_3O^+}}{\alpha_{H_2O} \times \gamma_{EtOH_2^+}} = 1$ the values in the last column of Table 4 become those of K. Aside from the fact that the values vary widely, they are much too large to agree with the calculations of Brönsted and Kolthoff.

Fig I. Plot of Distribution Ratios against Electrolyte Concentration

* indicates experiments so marked in tables.

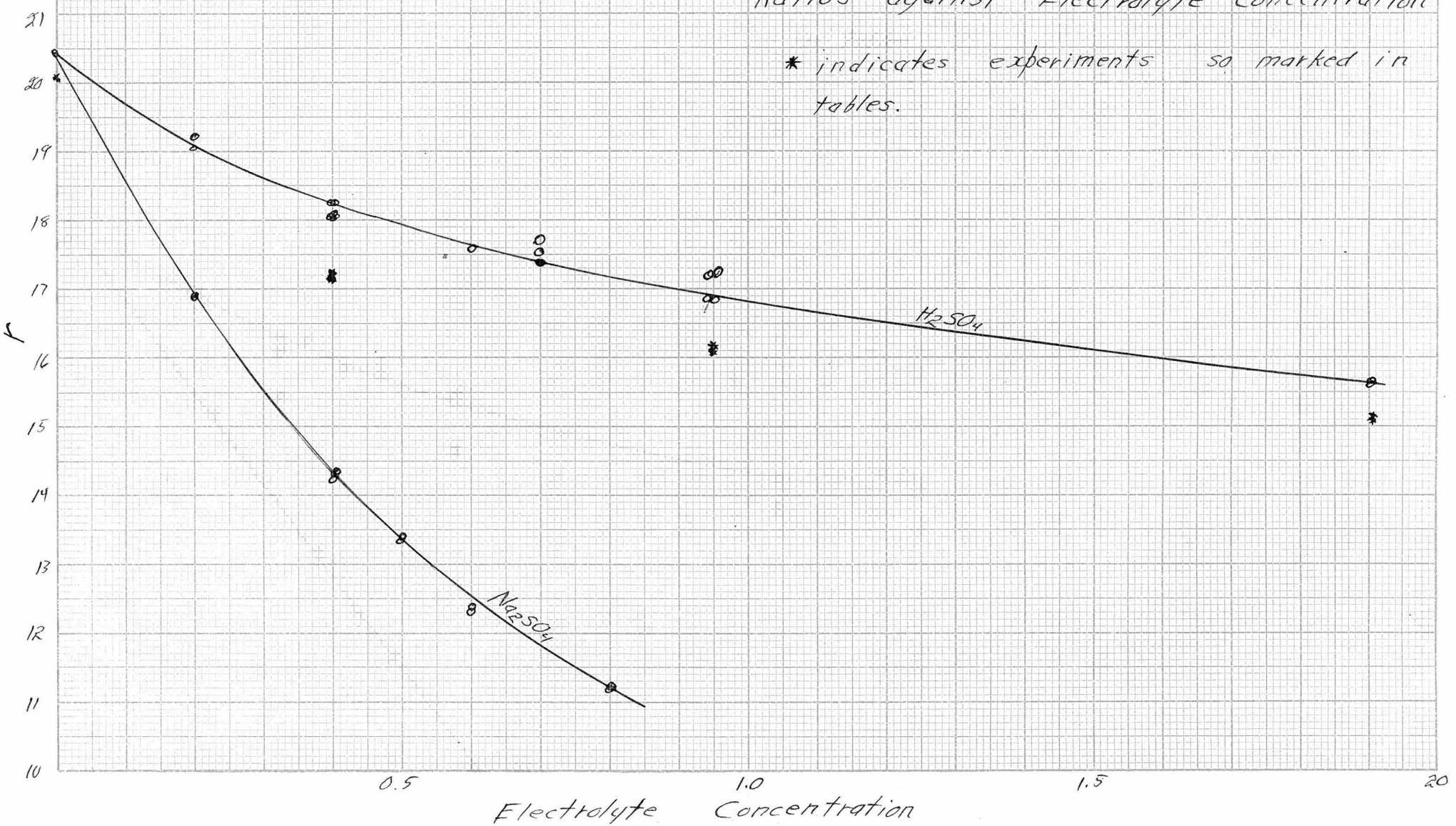

Fig 2. Plot of Distribution Ratio against Electrolyte Activity

* indicates experiments so marked in tables

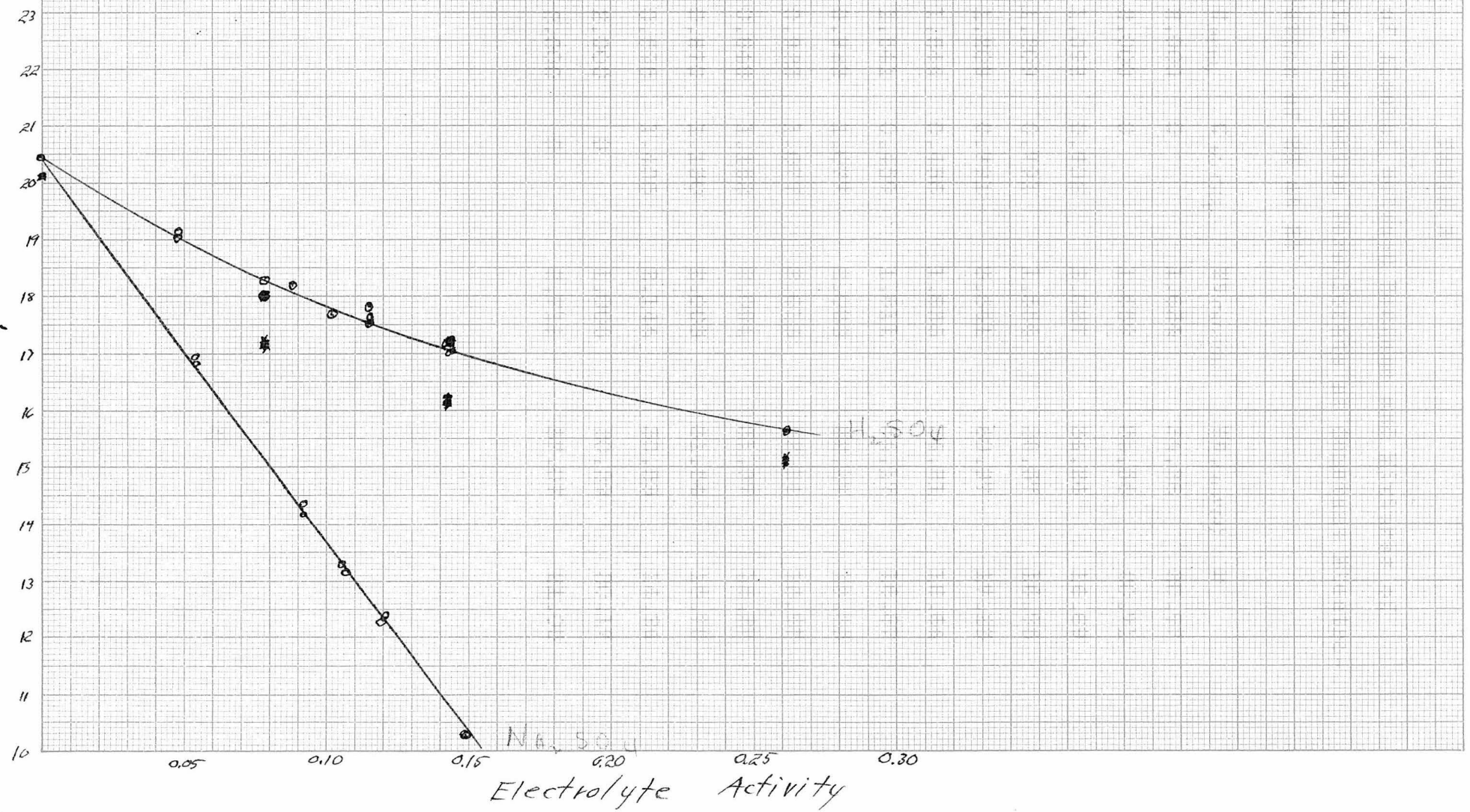

TABLE 3

Distribution of Alcohol between Benzene and Mixtures of Perchloric Acid and Sodium Perchlorate at Constant Electrolyte Concentration of 2N at 25°

No.	C_{HClO_4}	C_{NaClO_4}	$Wt_{EtOH(B)}$	$Wt_{EtOH(A)}$	r
1	2.000	0	1.634	34.28	20.97
2	2.000	0	1.659	34.36	20.71
3	1.098	0.902	2.027	34.24	16.89
4*	1.209	0.791	1.556	26.37	16.95
4a*	1.209	0.791	3.541	60.97	17.23
5	1.544	0.456	1.836	34.21	18.64
6	1.541	0.459	1.811	34.17	18.87
7	0.923	1.077	2.033	32.17	15.83
8	0.923	1.077	2.013	32.14	15.97
9	0.848	1.152	2.094	31.97	15.27
10	0.870	1.130	2.003	31.54	15.75
11	0.595	1.405	2.144	30.53	14.24
12*	2.000	0	1.006	20.29	20.17
13*	2.000	0	2.711	57.07	21.05

TABLE 4

Apparent Equilibrium Constants of the Formation of $C_2H_5OH_2^+$ in Aqueous Sulfuric Acid at 25°

α	r_n	r_a	$\frac{f_{EtOH(W)} \gamma_{H_3O^+}}{a_{H_2O} \gamma_{EtOH_2^+}}$ K
0.05	17.1	19.0	1.11
0.10	13.7	17.8	1.50
0.15	10.3	16.9	2.13

In Table 3 the first column gives the experiment number. The second gives C_{HClO_4}, the concentration of perchloric acid. The third gives C_{NaClO_4}, the concentration of sodium perchlorate. The fourth gives $Wt_{EtOH(B)}$ the weight of alcohol per liter in the benzene phase. The fifth gives $Wt_{EtOH(A)}$ the weight of EtOH per liter in the aqueous phase. The sixth gives the distribution ratio. In most of these experiments the amount of alcohol is from 30.5 - 34.2 g. per liter. In a few experiments (marked with an * in the table) the amount of alcohol was much greater or smaller.

Fig. 3 shows the distribution ratio plotted against the acid concentration. With the exception of the point corresponding to experiment 14 they all fall close to a straight line, a condition necessary in order that $K \frac{\gamma_{EtOH}\,\gamma_{H_3O^+}}{\alpha_{H_2O}\,\gamma_{EtOH_2^+}}$ should be constant. The value of r_n was found by extrapolation to zero acid concentration. From equation (6) we have

$$K \frac{\gamma_{EtOH}\,\gamma_{H_3O^+}}{\alpha_{H_2O}\,\gamma_{EtOH_2^+}} = \frac{r_a - r_n}{r_n \times C_{H_3O^+}} \qquad (7($$

But $(r_a - r_n)/C_{H_3O^+}$ is the slope of the curve in Fig. 3 and its value is equal to 0.467. The value of $K \frac{\gamma_{EtOH}\,\gamma_{H_3O^+}}{\alpha_{H_2O}\,\gamma_{EtOH_2^+}}$ is therefore equal to 0.406. This value holds for the entire range of acid concentrations. However, the value is too large to agree with the calculations of Brönsted and Kolthoff. The values obtained by these authors are based on more reliable methods than that used here. It is therefore probable that $\frac{\gamma_{EtOH}\,\gamma_{H_3O^+}}{\alpha_{H_2O}\,\gamma_{EtOH_2^+}}$ has a large numerical value, and that the apparent equilibrium constants are much larger than the true equilibrium constant.

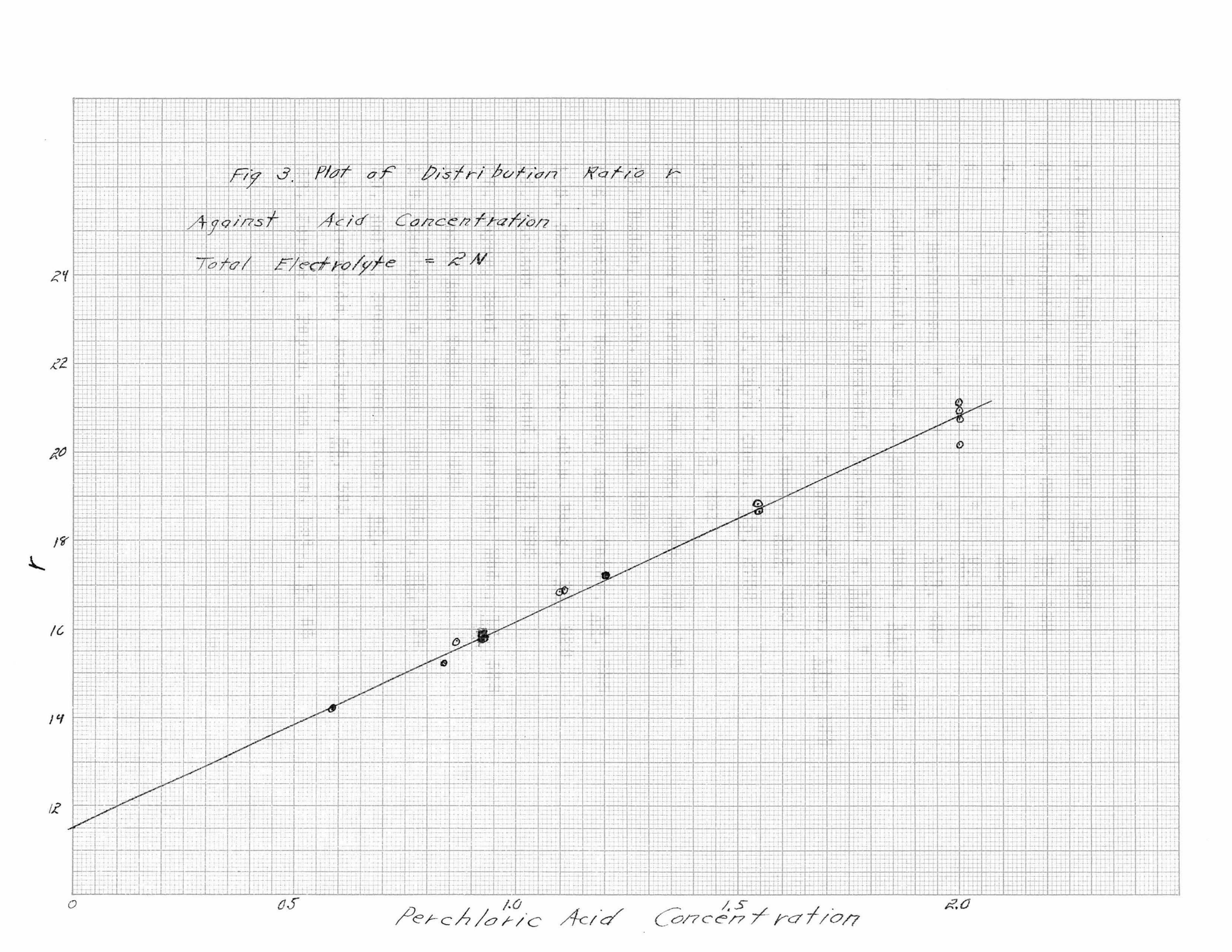
Fig 3. Plot of Distribution Ratio r
Against Acid Concentration
Total Electrolyte = 2N
24
22
20
18
16
14
12
r
0
0.5
1.0
1.5
2.0
Perchloric Acid Concentration

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11 THE HYDRATION OF ACETYLENE

SUMMARY

1. It has been established that oxygen exerts an inhibiting effect in the formation of the complex compound s of mercury which catalyze the hydration of acetylene.

2. The hydration of acetylene has been shown to be of first order with respect to acetylene.

3. The conditions for the rapid determination of acetylene in the presence of oxygen by the bromate-bromid e method have been determined.

INTRODUCTION

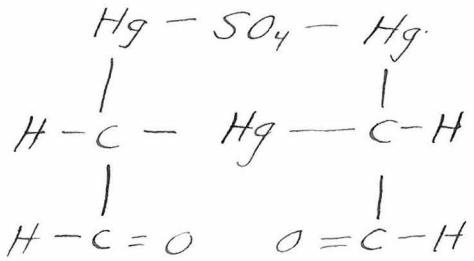
A well known industrial method for the production of acetaldehyd e involves the hydration of acetylene in sulfuric acid solutions containing mercuric sulfate.

$$C_2H_2 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO$$

During the reaction there is present an amorphous white precipitate. Other acids besides sulfuric acid likewise hydrate acetylene in the presence of their mercury salts. The reaction was discovered by Kutscheroff.[1]

The nature of the organic mercury compounds present as precipitates during the reaction is not known, but various investigators have proposed various formulas which agree with the empirical formulas[1-34]. Whitmore[35] indicates that the precipitate probably varies in composition with varying conditions of formation. He believes it probable that the organic mercury compounds are not the real catalysts but may be merely products of side reactions and that the hydration is catalyzed by mercuric ions in acid solution. Vogt and Nieuwland[34] pointed out that it is impossible to detect any inorganic salts of mercury in the catalytic mixture after the absorption of acetylene. They propose the following mechanism and structure.

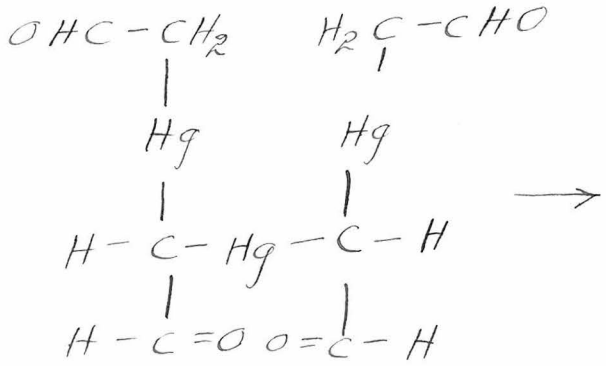
$$3\,HgSO_4 + 2\,C_2H_2 + 2\,H_2O \longrightarrow$$



$+ 2\,H_2SO_4$

A

$A + 2\,C_2H_2 + 2\,H_2O \longrightarrow$



$\longrightarrow$

$A + 2\,CH_3CHO$

In view of the importance of the reaction it is strange that nothing can be found in the literature concerning the reaction rates and the factors influencing them. Vogt and Nieuwland[34] have measured the rates of absorption of acetylene during and subsequent to the formation of the catalyst. Their data was not published, but they discussed it qualitatively. It should be noted that rate of absorption is not necessarily a measure of rate of reaction.

This research was undertaken to determine the reaction rates and the factors influencing them.

EXPERIMENTAL

PRELIMINARY EXPERIMENTS. It is obviously desirable that in determining the reaction rates, the reaction should be carried out without the presence of a precipitate. Vogt and Nieuwland[34] have shown that the reaction procedes most rapidly with those acids whose corresponding mercury-acetylene derivatives are most soluble in excess acid, e.g., sulfuric acid and perchloric acid.

When qualitative experiments were made to determine the limits of the concentration of the sulfuric acid and mercuric sulfate that could be used, it was found that on passing purified acetylene into 6-10 normal sulfuric acid, turbidities were formed even when the concentration of mercuric sulfate was carried so low that no acetaldehyde could be detected with 2, 4-dinitrophenylhydrazine reagent (1 gram 2, 4-dinitrophenylhydrazine in 100 ml. concentrated H_2SO_4) even after keeping the solution saturated with C_2H_2 for 2 - 4 hours.

Davis, Crandall, and Higbee[x] have shown that oxygen interferes with the bromination of acetylene and that aluminum, nickel, and mercuric salts catalyze the bromination. It was thought probable, therefore, that oxygen may also inhibit the hydration of acetylene. An attempt to hydrate acetylene by boiling a 6n sulfuric acid solution, cooling it in an atmosphere of pure acetylene, freed from oxygen by passing it through two spiral wash bottles containing alkaline pyrogallol and a third containing chromous chloride, and finally saturating the solution with the acetylene. No acetaldehyde could be detected with

the 2, 4-dinitrophenylhydrazine reagent. When the same procedure was followed with 6n sulfuric acid containing mercuric s ulfate, that acetaldehyde was formed without the formation of a precipitate, even when mercuric sulfate concentrations were carried as high as 0.001 M. It has thus been established that oxygen plays a role in the hydration of acetylene.

MATERIALS AND SOLUTIONS. Acetylene was prepared from calcium carbide using alcohol and water according to the method of Mathew[37] and purified by passing through two spiral wash bottles containing solutions made up of 15.6 parts $Cu_2SO_4 \cdot 5H_2O$, 5 parts dilute H_2SO_4 acid (1:4) and 100 parts water. These were followed by either a third spiral wash bottle containing 6n sodium hydroxide or in case oxygen was to be removed two spiral wash bottles containing alkaline pyrogallol. In some cases a fifth wash bottle containing chromous chloride was used.

Solutions of mercuric salts were prepared by boiling Baker's U.S.P. red mercuric oxide with as little acid as would dissolve it. In the case of standard mercuric sulfate solutions, the solution, after cooling, was made up to the desired volume in a volumetric flask.

Acid solutions were standardized against recrystallized borax.

The standard potassium bromate-bromide solution was made 0.05000N in potassium bromate and 0.10N in potassium bromide.

Sodium thiosulfate was standardized against the potassium bromate-bromide solution, blanks being run daily.

METHOD OF ANALYSIS. For the purpose of this research a rapid and accurate method for the determination of acetylene in solution is essential. None of the methods appearing in the literature are either rapid enough or accurate enough. It was decided to take the potassium bromate-bromide method as a basis for developing a suitable method.

Davis, Crandall, and Higbee[36] have shown that oxygen interferes in the determination of acetylene by bromination and described a procedure for excluding oxygen. Their method is too long however, and of doubtful accuracy. They point out that aluminum, nickel, and mercuric salts aid in the quantitative bromination of acetylene. Aluminum and nickel proved to be entirely unsatisfactory.

With mercuric salts it was observed that satisfactory results could be obtained only when an amount of mercury in excess of total halide is present, but with an excess of mercury the endpoint in the iodometric determination of the excess bromine is uncertain. This was satisfactorily remedied by adding sodium chloride or hydrochloric acid before adding the potassium iodide.

The procedure which gave the best results is as follows; A vacuum flask of the type used by Davis, Crandall, and Higbee containing 10.00 ml. of 0.05N $KBrO_3$-K Br solution is evacuated and the following added in order: 5 ml. of dilute sulfuric acid, 5 ml. of 0.1f mercuric sulfate, 50 ml. water, sample. The flask is then shaken 4 - 5 minutes, and then 5 ml. of 1f sodium chloride is added, followed by 1g. of potassium

iodide in 10 ml. water. The liberated iodine is then titrated with 0.02N sodium thiosulfate. A blank is run at the same time.

To test the method a nearly saturated solution of acetylene was prepared and stored in the apparatus subsequently used to carry out the hydration of acetylene. Samples were drawn by means of pipetts of various sizes. It was found that the bromine used up was proportional to the volume of the pipetts, within the limits of the titration error.

Since acetaldehyde is slowly oxidized by bromine it is necessary to remove it or make a correction. It was found that acetaldehyde uses up about 1% as much bromine as the corresponding amount of acetylene. A large number of experiments were made to determine the practicability of oxidizing the aldehyde with sodium peroxide in alkaline solution and decomposing the excess peroxide with carbon, silver oxide, manganese dioxide, etc. The results were unsatisfactory and it was decided to apply a correction for the aldehyde instead of attempting to remove it.

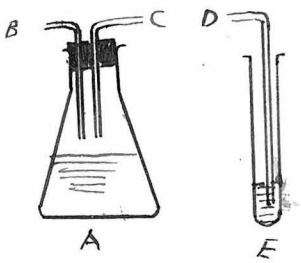


Fig. I

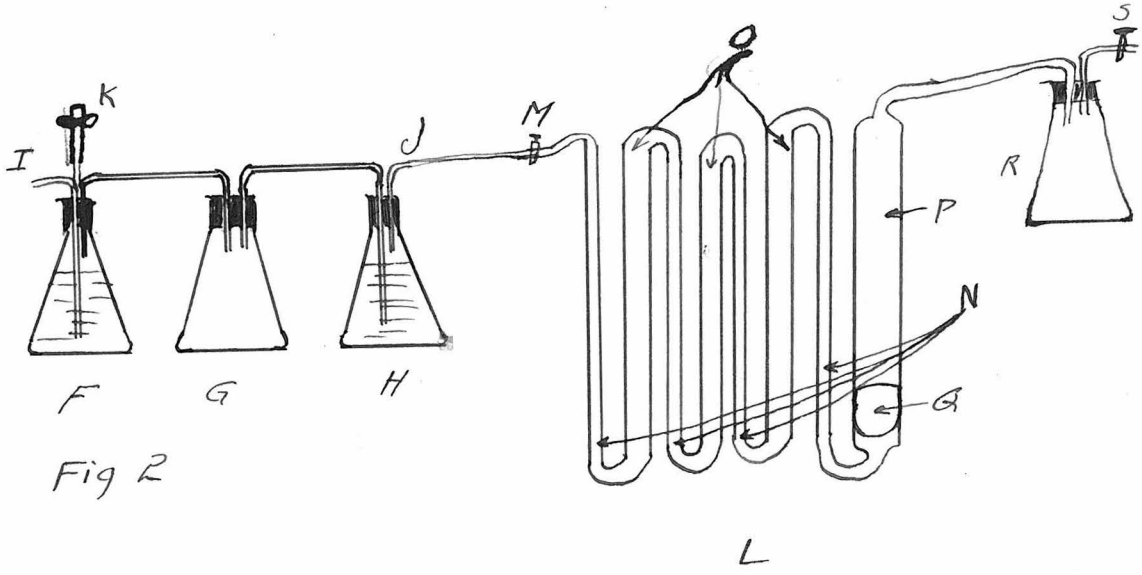


Fig 2

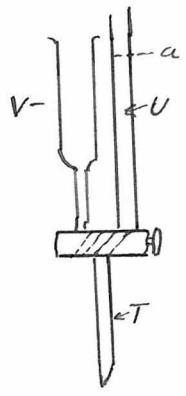


Fig. 3

DESCRIPTION OF APPARATUS AND PROCEDURE. Fig. 1 shows the apparatus in which the catalyst solution was prepared. The flask A was selected of such a size that the solution would leave a space of 50 ml. or less. The solution of sulfuric acid and mercuric sulfate, containing enough water to bring the acid concentration to about 50%, was introduced into this flask and slowly heated to boiling. Purified, oxygen-free acetylene was then passed into the flask through B; D was connected to C by a short piece of rubber tubing and the boiling continued for 3 - 5 minutes. The flask was then cooled as rapidly as possible, and with as little agitation of the liquid as possible. The tube D dips into a little water in the test tube E and serves to prevent air being sucked into the flask through C. When the flask and contents had cooled to room temperature the flask was shaken until the solution had absorbed about half its volume of acetylene. The solution was then diluted to the desired weight (all concentrations being expressed on the basis of 1000 g. of water). The catalyst solutions were prepared in higher concentrations of acid and mercuric sulfate than the final solutions were to be, as it was found that when an attempt was made to prepare the catalyst in dilute acid solution, considerable reduction of mercury took place. This was due to the solution absorbing small amounts of C_2H_2 as soon as the boiling was stopped, and the aldehyde produced reduced the mercury at the high temperature.

The hydration was carried out in the apparatus shown in Fig. 2. Flask H contained 400 ml. of water at the start. The entire apparatus was filled with acetylene by passing a stream of purified gas through it for several hours, the gas

entering at I. The catalyst solution was then introduced through K, and, while continuing to pass acetylene into the apparatus the solution was saturated with the gas by shaking F. At this point varying degrees of turbidity (usually small) appeared. The significance of this is discussed below. I was then connected to M in place of J and the solution was forced into L (vol. 250 ml.) by applying pressure at J with an atomizer bulb. The liquid flowed down the four small vertical tubes N (30 cm. x 5 mm. bore) and up the three large vertical tubes O (30 cm. x 10 mm. bore,) and finally filled the large vertical tube P (30 cm. x 20 mm. bore) in which the float Q fitted snugly. About 150 ml. of solution was forced into flask R in order to wash out any liquid which had lost acetylene to the air. By this means L was filled with the solution to be examined. The apparatus was designed to permit withdrawals of samples of the solution without appreciable change in composition. The float minimized the diffusion of acetylene into the air space above it and the long narrow tubes minimized diffusion of acetylene into the less concentrated solution under the float. The apparatus was kept in a thermostat at 25.00± 0.05℃.

Sampling was accomplished by means of the pipette illustrated in Fig. 3. This was made out of a 3-way stopcock. It contained 3.21 ml. at 25 . It was cleaned and dried and then filled by attaching it, by means of a short length of rubber tubing, to M which was kept closed while air was being forced into R, the pressure being conserved by closing S. On opening M, solution was forced into T and up into U up to

level a. In this way all solution which may have lost acetylene by contact with the air in T is washed into U. The stopcock is closed, and A is attached to the vacuum flask used in the analysis. About 15 ml. water is placed in V, and the solution is washed into the vacuum flask.

At the end of every run samples were drawn for titration with standard sodium hydroxide.

RESULTS AND DISCUSSION

The integrated first order reaction rate expression for the hydration of acetylene is given in equation (2)

$$2.303 \log C_o/C_f = k\,t \qquad (2)$$

where C_o is the initial concentration of acetylene C_f is the concentration at time t (expressed in hours), and k is the s pecific reaction rate constant.

The experimental date for a typical run is shown in Table 1. In this table the first column gives the reaction time t in hours, the second gives the volume of sodium thiosulfate used up, the third gives the volume of thiosulfate corrected for the effect of acetaldehyde, the fourth column gives the value of 2.303 log C_o/C_f, and the fifth gives the value of k.

The values obtained show that k is of first order with respect to acetylene concentration.

TABLE 1

Hydration of Acetylene in 1M H_2SO_4 and 0.00025 M H_2SO_4

at 25 Run # 5

t	$V_{Na_2S_2O_3}$	$V'_{Na_2S_2O_3}$	2.303 log C_o/C_t	k hrs^{-1}
0	6.88	6.88	0	
0.467	6.37	6.36	0.0786	0.0168
1.600	5.25	5.23	0.274	0.173
3.250	4.00	3.97	0.551	0.169
4.27	3.33	3.29	0.738	0.173
5.28	2.91	2.86	0.879	0.167
			Mean	0.170

An easier and more accurate evaluation of k is the slope of the curve obtained by plotting log C_o/C_t against t (Fig. 4). It is observed that in all cases straight lines were obtained.

In Table 2 are listed the constants calculated from Fig. 3 along with the results of several other runs. The first column gives the run number, the second gives the acid concentration, $M_{H_2SO_4}$ in mols per 1000g. water, the third gives M_{HgSO_4}, the concentration of mercuric sulfate in mols per 1000g. water, the fourth column gives k specific reaction rate constants.

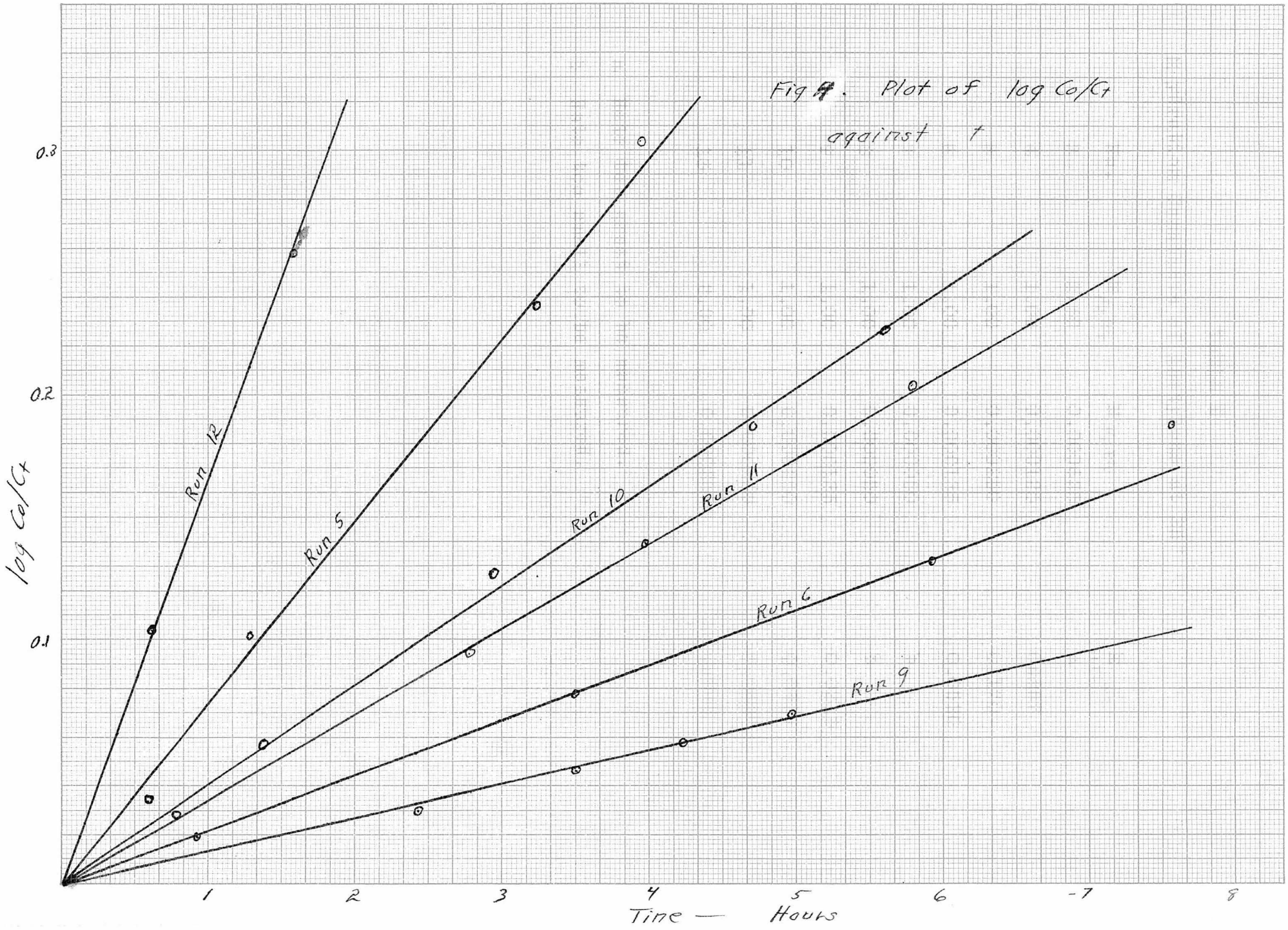


Fig 4. Plot of log Co/Ct against t
0.3
0.2
0.1
log Co/Ct
Run 12
Run 5
Run 10
Run 11
Run 6
Run 9
1
2
3
4
5
6
7
8
Time — Hours

TABLE 2

Hydration Constants of Acetylene at 25°

No.	$M_{H_2SO_4}$	M_{HgSO_4}	$k_{hrs^{-1}}$
3	2.50	0.000625	a
4	1.00	0.000125	0.0287
5	1.00	0.000250	0.170
6	1.00	0.000125	0.0520
7	1.00	0.000050	b
8	1.00	0.000050	b
9	1.00	0.000125	0.0315
10	1.00	0.000250	0.0937
11	1.00	0.000250	0.0805
13	2.00	0.000250	0.383

a Rate too great to be measured.

b Rate too small to be measured.

An inspection of Table 2 shows runs in which acid and mercuric sulfate concentrations were duplicated do not yield duplicate values of k. The differences are too great to lie within the limits of error of the various measurements. The explanation doubtlessly lies in the turbidities observed when the solutions were saturated with acetylene in C, Fig. 2. This indicates that the reaction by which the catalyst is formed is reversible to some extent. In the high concentration of sulfuric acid and mercury sulfate in which the catalyst is prepared in A, Fig. 1, the hydration of the acetylene takes place at a very great rate. It would seem that the acetylene is used up in a very short time and then the reaction by which the catalyst is prepared would take place in the reverse direction to a greater or less extent. Since oxygen has not been completely excluded from the apparatus of Fig. 2, its inhibiting effect would assert itself. That oxygen probably does not have an inhibiting effect in the actual hydration but only in the formation of the complex compound which serves as the catalyst has been demonstrated by an experiment in which the catalyst was prepared in A, as described above, and oxygen was then introduced in small amounts along with the acetylene; no precipitate was observed.

Apparatus and technique is now being worked out which will enable the solution to be prepared entirely in the absence of oxygen.

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